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<p>(21) International Application Number: PCT/GB89/00980 (22) International Filing Date: 23 August 1989 (23.08.89) (30) Priority data: 8820100.9 24 August 1988 (24.08.88) GB (71)(72) Applicant and Inventor: WILLMORE, Peter, John [GB/ GB]; 15 Brookleigh Avenue, Mancot, Deeside, Clwyd (GB). (74) Agent: ROYSTONS; Tower Building, Water Street, Liver- pool L3 1BA (GB). (81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI pa- tent), BR, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (Eu- ropean patent), DK, FI, FR (European patent), GA (OA- PI patent), GB, GB (European patent).</p>		<p>HU, IT (European patent), JP, KP, KR, LK, LU, LU (Euro- pean patent), MC, MG, ML (OAPI patent), MR (OAPI pa- tent), MW, NL, NL (European patent), NO, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US.  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: DECORATION OF SUBSTRATES  (57) Abstract  A composition for applying to substrates to impart a thermochromic effect comprises one or more thermochromic sub- stances, typically microencapsulated nematic liquid crystals, in an aqueous, typically acrylic based binder.</p>		

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Title: Decoration of Substrates

#### DESCRIPTION

5 This invention concerns the decoration of substrates particularly but not exclusively fibres and fabrics.

It is of course, well known to decorate fibres or fabrics by applying colours randomly or in a pattern thereto, such as by screen printing. The colours are, therefore, fixed.

10 Attempts have been made to decorate fabrics with thermochromic substances, i.e. substances which change colour with changes in temperature. Such substances have been incorporated in resins and applied to a variety of substrates but so far attempts to apply such  
15 to fabrics have been unsatisfactory largely due to the poor handle or feel of the resultant fabric, poor wash resistance and poor visibility of the resultant colour change effect.

20 An object of this invention is to provide a composition for decorating a substrate whereby the decorated substrate exhibits a thermochromic effect.

Another object of this invention is to provide a

substrate, such as a fibre or fabric, having a thermochromic effect.

A further object of this invention is to provide a method of producing a substrate, such as a fibre or fabric, having a thermochromic effect.

According to a first aspect of this invention there is provided a substrate, such as a fibre or fabric, having a coating thereon of a composition comprising one or more thermochromic substances and a binder.

According to a second aspect of the invention there is provided a composition for decorating a substrate, the composition comprising one or more thermochromic substances and a binder.

According to a third aspect of the invention there is provided a method of producing a substrate, such as a fibre or fabric, having a thermochromic effect comprising the step of applying to the substrate a composition comprising one or more thermochromic substances in a binder.

The thermochromic substance and binder may be mixed in any suitable ratio but preferably in the range of 3:2 to 2:3 by volume especially about 1:1.

The invention may be used on a variety of substrates including fibres or yarns, fabrics,

preferably woven fabrics, paper, plastics and any other suitable material.

The choice of binder is believed to be fairly important and preferred binders have one or more of the following properties;

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1. Substantial optical clarity when dried or cured;
2. Wash resistance when dried or cured for laundering;
3. Flexibility;
4. Colourlessness;
5. Aqueous based or at least having no low molecular weight organic solvents or chemicals which might damage the thermochromic substance or substances;
6. Sufficient strength to remain adhered to the fibre or fabric during use and washing; and
7. Capable of allowing a fabric to breathe.

Various binders may fulfill most if not all of the above desired properties. Suitable binders include aqueous, preferably cross-linkable, polymer emulsions. The polymer could be polyurethane, acrylic, polyvinyl acetate or polyvinyl chloride but it will be appreciated that other polymers may prove to be

satisfactory for use in the invention.

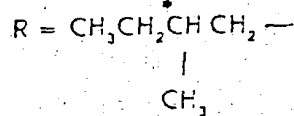
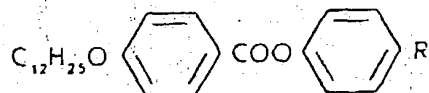
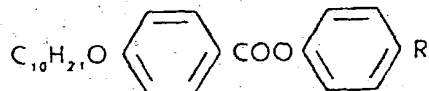
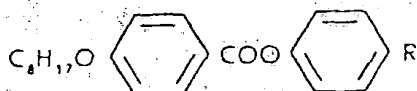
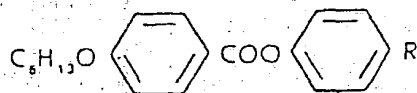
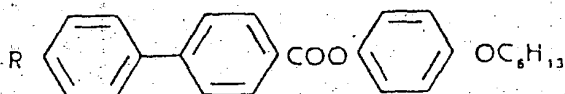
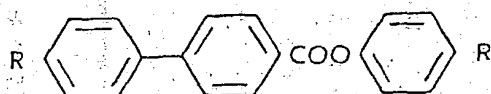
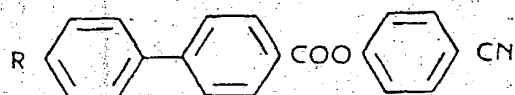
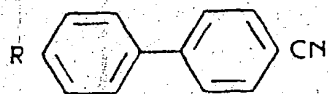
Preferred binder systems are based on acrylic and methacrylic polymers and copolymers produced by the emulsion or dispersion method in water. Suitable acrylic and methacrylic monomers for such binders include ethyl acrylate, butyl acrylate, methyl methacrylate and acrylonitrile as main ingredients and acrylamide, methylol acrylamide, acrylic acid and methacrylic acid as minor ingredients.

10 A particularly useful group of binders for compositions of the invention comprise in percent by weight of copolymer

	Butyl acrylate	80 - 100
	Acrylonitrile	2.5 - 20
15	Methylol acrylamide	1 - 3
	Methacrylic acid	1 - 3

The preferred thermochromic substances to be used in the present invention include nematic liquid crystals, cholesteric liquid crystals and smectic liquid crystals. Preferably microencapsulated chiral nematic liquid crystals suspended in aqueous medium will be used in the invention. Various types of suitable thermochromic substances are disclosed in U.K. Patent Specifications Nos. 1556994, 1592161, 1596012, 25 1596013, 1596014 and 1603076.

Typical chiral nematic compounds have the following formulae:



The thermochromic substances used in the present invention will preferably exhibit several colour changes over a range of temperatures, typically -30 to 150 degrees Celsius and preferably such as produced by contact with the body. The thermochromic substances may be colourless or black and typical colour changes may be from colourless or black to tan to red to green to blue. Two or more thermochromic substances may be used which change colour at different temperatures so that a mixture of colour changes may be produced.

The method of the invention may be used on individual fibres, fabrics prior to making up into a garment or other article and the finished article itself. Preferred fibres and fabrics will be black, although darker coloured substrates have also been found to be suitable. Paler coloured substrates may also be used by first overprinting with a darker, preferably black layer. They may also advantageously be fine, thin or supple. Suitable fabrics include polyesters, silks and chiffons.

The compositions used in the invention may be applied to fibres and fabrics in any suitable way, such as by printing, including screen printing, spraying, dipping, brushing and laminating. The compositions used in the invention may be applied all over a fabric



or to discrete areas thereof.

The compositions used in the invention may include further substances such as processing aids for the method of application to be used. Other additives may include U.V. stabilisers, anti foaming agents, surfactant stabilisers, antioxidants, thickeners and fire retardant substances.

The invention may provide a means of producing a clearly defined, clearly visible thermochromic effect on a variety of substrates.

The invention will now be further described by means of the following Example.

#### EXAMPLE

A composition for coating a fabric was produced by mixing 50 parts by volume of Licritherm suspension TCC 216 (Microencapsulated chiral nematic liquid crystal supplied by BDH Limited) with 50 parts by volume of an aqueous acrylic emulsion.

The composition was used to coat a black fabric and the resultant coated fabric exhibited colour changes with the changes in temperature from skin contact with the fabric and from breathing on the fabric.

## CLAIMS

1. A composition for decorating a substrate comprising one or more thermochromic substances and a binder.
- 5 2. A composition as claimed in claim 1, wherein the thermochromic substance and binder are present in a ratio by volume of from 3:2 to 2:3.
3. A composition as claimed in claim 1, wherein the volume ratio of thermochromic substance to binder is  
10 about 1:1.
4. A composition as claimed in claim 1, 2 or 3, wherein the binder is an aqueous polymer or copolymer.
5. A composition as claimed in claim 4, wherein the binder is an aqueous acrylic or methacrylic polymer or  
15 copolymer.
6. A composition as claimed in claim 5, wherein the binder comprises one or more of ethyl acrylate, butyl acrylate, methyl methacrylate and acrylonitrile.
7. A composition as claimed in claim 6, wherein the  
20 binder further comprises one or more of acrylamide, methylol acrylamide, acrylic acid and methacrylic acid as minor ingredients.
8. A composition as claimed in claim 5, 6 or 7

wherein the polymer content of the binder comprises is percent by weight:

	Butyl acrylate	80 - 100
	Acrylonitrile	2.5 - 20
5	Methylol acrylamide	1 - 3
	Methacrylic acid	1 - 3

9. A composition as claimed in any one of claims 1 to 8, wherein the thermochromic substance comprises nematic liquid crystals.

10 10. A composition as claimed in claim 9, wherein the thermochromic substance comprises an aqueous suspension of microencapsulated nematic liquid crystals.

11. A composition as claimed in any one of claims 1 to 10, wherein the thermochromic substance or  
15 substances exhibit two or more colour changes over temperatures in the range -30 to 150 degrees C.

12. A composition as claimed in any one of claims 1 to 11, further comprising one or more of U.V. stabilisers, anti foaming agents, surfactant  
20 stabilisers, antioxidants, thickeners and fire retardants.

13. A composition as claimed in any one of claims 1 to 12, in the form of a printing ink.

14. A method of producing a substrate having a  
25 thermochromic effect comprising the step of applying to

the substrate a composition as claimed in any one of claims 1 to 13.

15. A substrate having a coating thereon of a composition as claimed in any one of claims 1 to 13.

5 16. A substrate as claimed in claim 15, wherein the substrate is a fibre or fabric.

17. A substrate as claimed in claim 15, comprising woven fabric.

10 18. A substrate as claimed in claim 15, comprising paper.

19. A composition as claimed in claim 1 and substantially as hereinbefore described with reference to the foregoing Example.

15 20. A method as claimed in claim 14 and substantially as hereinbefore described with reference to the foregoing Example.

21. A substrate as claimed in claim 15 and substantially as hereinbefore described with reference to the foregoing Example.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 89/00980

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>5</sup> : B 44 F 1/00, C 09 K 19/00, C 09 D 11/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System <sup>1</sup>	Classification Symbols	
IPC <sup>5</sup>	B 44 F, C 09 K, G 02 F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No <sup>13</sup>
X	Patent Abstracts of Japan, vol. 9, no. 207 (P-382)(1930), 24 August 1985 & JP, A, 6069629 (SHINWA SEISAKUSHO K.K.) 20 April 1985, see the abstract	1
Y	--	9,10,15
Y	Surface Coatings Australia, vol. 24, January/February 1987, S. Glade: "Thermochromic paints", pages 8,9, see the whole article & Chemical Abstracts, AN no. 107-060710 --	1,9,10,13
Y	Chemical Abstracts, Data Base, AN no. 091-176399 & JP, B, 7983937 (SHIBANAI) 4 July 1979, see the whole abstract --	1,5,9,10, 13
Y	Chemical Abstracts, Data Base, AN no. 080-097526 & JP, A, 7383903 (TOKYO OHKA KOGYO) ./.	1,9,10,13
<p>* Special categories of cited documents: <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
21st November 1989	09.01.90	
International Searching Authority	Signature of Authorizing Officer	
EUROPEAN PATENT OFFICE	T.K. WILLIS	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	CO., LTD) 8 November 1973, see the whole abstract	
	--	
Y	Patent Abstracts of Japan, vol. 11, no. 71 (M-567) 4 March 1987 & JP, A, 61227085 (OIKE KOGYO K.K.) 9 October 1986	1,10,14
	--	
Y	US, A, 3802945 (B.G. JAMES) 9 April 1974, see column 1, lines 5-13; column 2, lines 12-19; column 3, lines 43-64; claims 1-7	1,5,9,10,15
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 8900980  
SA 30779

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 22/12/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3802945	09-04-74	None	